

Susceptibility to Local Breakdown of Passive Film Formed on Iron

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The measurement of electrochemical reactivities at local sites of passive films which sustain the corrosion resistivities of the substrate metals is important for a better understanding of precursor process of localized corrosion. The authors have developed a liquid-phase ion gun (LPIG) technique to generate locally small amount of Cl^- ions and applied to induce the local breakdown of passive films on iron [1]. The local breakdown processes by a LPIG was classified into three domains as follows.

I) induction: The film is still passive in spite of the local enrichment of Cl^- ions.

II) breakdown: The local breakdown of film is initiated and the positive feedback in which Fe^{3+} ions originated from the film are reduced at a LPIG microelectrode and Fe^{2+} ions from the microelectrode are oxidized at the breakdown site of the film is operative.

III) propagation: The bare iron surface is exposed to the solution and active dissolution as Fe^{2+} ions proceeds at the breakdown site.

In this study, the domain I, that is, the induction process for local breakdown of the passive film due to Cl^- ions, was investigated in detail with a LPIG.

The experimental procedures have been described elsewhere [1]. An iron plate with a purity above 99.99 % was employed for this experiment. The iron surface was mechanically polished with $\alpha\text{-Al}_2\text{O}_3$ abrasives down to 0.05 μm . Furthermore, the surface was etched in 5 vol% HNO_3 ethanol solution to make the substrate grains distinct. After the iron specimen was cathodically reduced in deaerated pH 6.5 borate solution to remove an air-formed film, it was anodically polarized at 0.7 V (SHE) for 1800 s in the renewed solution to form passive film. A silver microelectrode with a diameter of 50 μm covered by silver chloride film was employed as a LPIG microelectrode. The microelectrode was located above the passivated iron electrode. The distance between the microelectrode and passivated iron electrode was kept at 40 μm . The current of the microelectrode, I_{ME} , was changed stepwise from 0.1 nA to -8 μA to generate Cl^- ions, while the potential of the iron specimen was kept at 0.7 V (SHE) during generation of chloride ions.

An electron transfer reaction of redox species took place more feasibly on the iron {110} or {111} grain with thinner passive film than on the {100} grain with thicker passive film [2]. Here, the dependence of the initiation of local breakdown on the substrate grain was investigated by using the passivated iron electrode with distinctive crystal grains. A galvanostatic generation of Cl^- ions has a merit to keep constant the concentration of Cl^- ions during LPIG operation. Fig. 1 shows the typical transients of potential, E_{ME} , of the LPIG microelectrode (a diameter of 50 μm) and of current, I_{IE} , flowed through the iron electrode after the current step of the microelectrode from 0.1 nA to -8 μA in pH 6.5 borate solution. The iron electrode was passivated at 0.7 V (SHE) for 1800 s in pH 6.5 borate solution after the chemical etching. The orientation of the substrate grains was confirmed by an etch-pit method described previously [2]. After the

cathodic current step, E_{ME} tends to keep about 0.15 V (SHE) due to generation of Cl^- but shifts to the anodic direction when I_{IE} increases rapidly, i.e., the local breakdown is initiated. The induction period, t_{BD} , depends on the substrate grain. The induction period, t_{BD} , becomes longer in the order of the grains {110}<{111}<{100} which is the same in the order of film thickness evaluated previously [2]. It is clear that the local breakdown is initiated with the shorter time for the thinner film. This is also consistent with the least protective film on Armco iron {110} plane reported by Kruger [3].

References

1. K. Fushimi, K. Azumi, and M. Seo, *J. Electrochem. Soc.*, **147**, 552 (2000).
2. K. Fushimi, K. Azumi, and M. Seo, *ISIJ Int.*, **39**, 346 (1999).
3. J. Kruger, *J. Electrochem. Soc.*, **106**, 736 (1959).

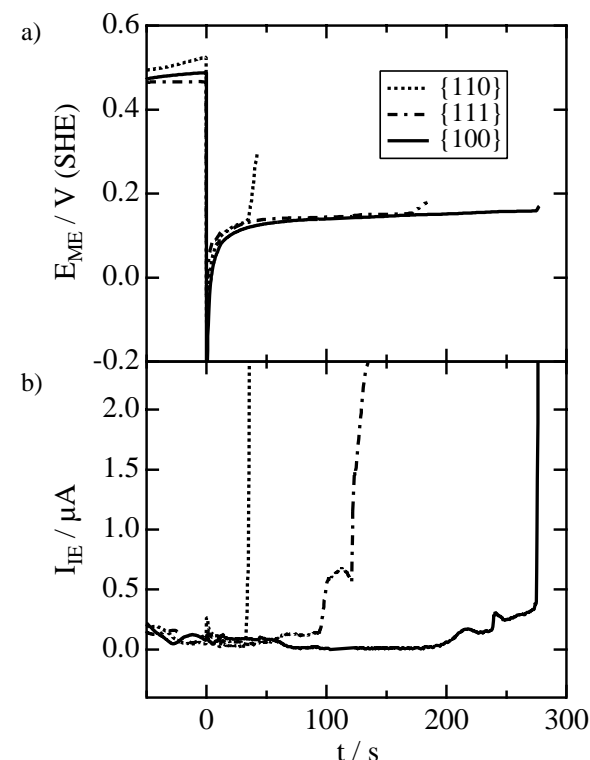


Fig. 1 Transients of a) potential, E_{ME} , of the LPIG microelectrode with a diameter of 50 μm and b) current flowed through the iron electrode, I_{IE} , after the current step of the microelectrode from 0.1 nA to -8 μA for a galvanostatic generation of Cl^- ions in pH 6.5 borate solution.

The iron electrode was passivated at 0.7 V (SHE) for 1800 s in pH 6.5 borate solution after the chemical etching. The LPIG was operated above each iron grain oriented to {110}, {111}, or {100} plane at a distance about 40 μm between LPIG and iron electrode.